RAW MATERIALS

ARGILLACEOUS MATERIALS IN THE SIBERIAN REGION

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The results of integrated studies of argillaceous materials of the Siberian Region are considered and recommendations are issued for evaluation of the quality of materials, which make it possible to identify the means of control of the main technological properties of argillaceous rocks with the aim of bringing then to the required level.

Despite the increasing share of engineering ceramics based on synthesized materials in the total ceramic production, argillaceous materials as yet are the most important for traditional materials, such as aluminosilicate engineering ceramics and refractories, porcelain (household and electroengineering), all types of faience, sanitaryware, etc.

Among argillaceous minerals, the most common are kaolinite (and its analogs) and minerals of the montmorillonite and hydromica groups. Kaolinite minerals make up finely disperse components of the best-quality and the rarest argillaceous rocks, i.e., white-burning (sometimes named "porcelain") refractory clays. Hydromica is the main clay-forming mineral used for ceramic sanitaryware and is sometimes found in refractory clay as the second argillaceous mineral. The montmorillonite group minerals are at the basis of low-melting clay and loams that are used, as a rule, for ceramics with tinted crock, including construction ceramics.

The Silicate Technology Department of Tomsk Polytechnic University has been researching Siberian clay for many years. The extensive accumulated database of experimental data makes it possible to speak of the Siberian School of Silicate Studies started by Prof. P. G. Usov who headed the Silicate Technology Department in 1943 – 1977. This school continues under his alumni.

The argillaceous materials of Siberia are represented by all varieties of argillaceous rocks: kaolins, plastic and kaolinic refractory clays, high-melting clays, low-melting clays, and loams.

The most promising white-burning refractory clays and kaolins for the ceramic industry in the Siberian Region are clays from the Aprelevskoe, Antonovskoe, Barzasskoe, and Kailinskoe deposits in the Kemerovo Region, Troshkovskoe,

Katomskoe, and Kamenskoe deposits in the Irkutsk Region, kaolin and refractory clays of the Kampanovskoe deposit in the Krasnoyarsk Region, Tuganskoe kaolin (the product of concentration of Tuganskoe kaolinized sand) in the Tomsk Region, etc. Among the high-melting clays, clay from the Voronovskoe and Aryshevskoe deposits in the Tomsk Region and Obskoe and Evsinskoe deposits in the Nobosibirsk Region have the most practical significance.

The depletion of domestic reserves of high-quality clays and kaolins forces the use of low-grade local argillaceous rocks in the ceramic industry. The available resources of such low-melting argillaceous materials, including those in Siberia, make them important for production of tinted-crock ceramics.

The diversity of argillaceous rocks in Siberia and their different behavior in the technological process makes it necessary to predict and control their main technological properties, which is impossible without the detailed study of such rocks.

The integrated evaluation of the clay materials implies the determination of some parameters such as chemical, granulometric, material compositions, structural specifics of the clay components, and physicochemical and technological properties. The chemical and material compositions of the argillaceous materials found in Siberia are indicated in Tables 1 and 2.

Clays are most frequently polymineral rocks and, accordingly, the chemical composition of clay (the gross chemical composition), although reflecting the specifics of the composition of all mineral components (argillaceous and non-argillaceous), does not always directly identify the types of minerals and their quantitative content.

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TABLE 1

Material	Weight content, %								
	SiO$_2$	Al$_2$O$_3$	TiO$_2$	Fe$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O	Δm_{calc}
Refractory clays									
Clay:									
Troshkovskoe	49.63	36.16[*]	–	2.57	0.95	1.30	0.40	0.12	8.93
Katomskoe	49.62	34.55	0.58	0.56	0.56	1.11	1.13[**]	–	12.70
Aprelevskoe	58.42	25.50[*]	–	2.97	2.10	0.50	1.48[**]	–	8.83
Barzasskoe	35.52	45.56	2.76	2.39	0.36	0.16	0.12[**]	–	13.20
High-melting clays									
Clay:									
Voronovskoe	57.57	26.44	0.75	1.60	1.28	0.94	0.74	0.87	9.81
Obskoe	57.57	24.86[*]	–	1.86	1.71	1.02	0.56	0.78	11.60
Evsinskoe	67.92	21.32	0.21	1.53	0.45	0.56	2.26	0.63	5.12
Kailinskoe	64.33	19.27[*]	–	2.02	1.43	1.54	0.91	0.51	9.90
Low-melting clay and loam									
Voroninskoe clay	62.64	13.77[*]	–	4.76	4.90	–	4.61[**]	–	9.32
Loam:									
Kornilovskoe	63.70	12.75[*]	–	5.16	3.50	3.48	2.99[**]	–	8.42
Yurginskoe	62.12	13.77[*]	–	4.76	4.20	0.99	4.72[**]	–	9.44
Rodionovskoe	62.96	13.26[*]	–	3.99	4.95	1.26	5.27[**]	–	8.31

[*] Content of (Al$_2$O$_3$ + TiO$_2$).

[**] Content of (K$_2$O + Na$_2$O).

TABLE 2

Clay	Argillaceous and finely dispersed component (below 5 μm)		Non-argillaceous component (above 5 μm)	
	mineral	weight content, %	mineral	weight content, %
Refractory clays				
Troshkovskoe	Kaolinite and halloysite	55.5	Quartz	10.0
			Feldspar	6.0
	Hydromica	4.7	Ferrous minerals	0.9
	Free quartz	8.0	Calcite and	
	Colloids	12.3	magnesite	2.5
High-melting clays				
Kailinskoe	Kaolinite	37.8	Feldspar	4.4
	Hydromica	14.4	Calcite	2.6
	Free quartz	37.1	Ferrous minerals	3.7
Low-melting clays				
Slyudyanskoe	Kaolinite, mont-morillonite, hydromica	28.7	Feldspar	26.0
			Gypsum	2.3
			Magnesite	3.6
	Free quartz	29.9	Limonite	8.5

However, some components in the chemical composition make it possible to predict the specifics of the mineralogical composition and properties of the particular rock. For instance, when the content of Al$_2$O$_3$ is above 30%, it points to a prevailingly kaolinite composition of argillaceous rock; from 20 – 30%, to hydromica (if the clay is monomineral) or to a mixture of hydromica and kaolinite (when the argillaceous component is polymineral); and less than 20%, to montmorilonite. The presence of Fe$_2$O$_3$ in quantities below 1% deter-

mines the white color of clay after firing, a quantity from 1 to 2% will impart yellowish tints to ceramics, and with the Fe$_2$O$_3$ content above 2% the color varies from yellow (3 – 4%) to red (above 4 %). The presence in the gross chemical composition of alkali metal oxides (Na$_2$O + K$_2$O) up to 1% with a prevailing kaolinite composition of finely disperse component will impede the process of clay sintering; when that content is over 1%, good sinterability is ensured while preserving high refractoriness.

The data on the granulometric composition of argillaceous rocks make it possible to identify the variety of argillaceous material (clay, loam, or loess) based on the ratio of sand, dust-like, and argillaceous articles and to predict its behavior in production. In particular, crack resistance and drying sensitivity of clays depend not only on their qualitative and quantitative mineralogical composition and the total content of natural grog (sand) particles, but also on the granulometry of these particles, since finely dispersed sand (below 0.25 mm) stops fulfilling the grog function typical of silica rocks, compacts the plastic clay mixture, and complicates the process of moisture transfer in drying. Furthermore, the content of clay particles (smaller than 5 μm) can be used to predict the suitability of clays for producing ceramics by casting of aqueous suspensions into porous molds. The practice established that argillaceous rocks with not more than 40% content of clay particles sized below 0.005 mm are not suitable for slip casting without a special plastifying additive, which is represented by another more disperse and plastic clay. This is especially significant in developing mixtures for red-burning majolica based on local low-melting clay and loam.

Since nearly all argillaceous rocks have a complex (polymineral) composition of the fine (argillaceous) fraction, identification of the mineral type of argillaceous material is rather complicated, labor-consuming, and possible only using up-to-date physicochemical analysis methods that enable one with sufficient accuracy to identify individual argillaceous minerals belonging to different types, and even discrete particles or interlayer accretions in mixtures. However, when these argillaceous minerals belong to the same group, their identification becomes rather problematic. This is mainly true of such common refractory clay minerals as kaolinite and halloysite, especially if the latter is represented by varieties with different degrees of hydration.

The fullest review of the method of diagnostics for halloysite is given by Sand and Ormsby [1], who concluded that the x-ray phase method is unsuitable for analysis of kaolinite-halloysite mineral mixtures. Brindly et al. [2] established that even 30% kaolinite in the mixture totally masks the presence of halloysite on the diffraction pattern. Preliminary physicochemical treatment of clays by organic liquids (for instance, impregnation with ethylene glycol or glycerin) expands the identification possibilities of thermal analysis, since they have been observed to form complexes with hydrohalloysite. This fact became the basis for qualitative determination of the presence of hydrohalloysite in mixtures with halloysite and kaolinite [3]. The invariability of the thermal effect position at $500 - 600°C$ on the derivatogram indicates that the sample is halloysite or kaolinite. Splitting of the effect in two points to a mixture of hydrohalloysite with halloysite, or with kaolinite, or with both. Thus, the presence of halloysite in different degrees of hydration (from metahalloysite to hydrohalloysite with intermediate forms of hydration) was registered in kaolinic varieties of Troshkovskoe and Katomskoe clays (Irkutsk Region) and in kaolin from the Zhuravlinyi Log deposit (Chelyabinsk Region) [4 – 6].

It has been reliability proved that the properties of clays are determined not only by their mineralogical compositions but also by the degree of crystallinity of clay-forming minerals. A certain degree of disruption in crystallinity is typical of all argillaceous minerals. This is more typical of montmorillonite and to a lesser degree of the kaolinite group of minerals. Opinion exists that structural disordering of argillaceous minerals is mainly due to isomorphic replacement in the octahedral (in the case of kaolinite [7]) or tetrahedral or in both types of layers simultaneously (which is most typical of montmorillonite [8]) by oppositely charged ions, which weakens the hydrogen bonds between the gibbsite and silica layers.

TABLE 3

Parameter	Clay variety			
	Glukhovetskoe kaolin	Troshkovskoe clay	Zhuravlinyi Log kaolin	Kailinskoe clay
Clay-forming mineral	Kaolinite	Kaolinite and halloysite		Kaolinite and hydromica
Ordering index	0.90	0.38	0.86	0.30
Particle size, μm	1.00 – 1.50	0.10 – 0.75	1.00 – 1.50	0.10 – 0.50
Wetting heat, J/g:				
in natural state	5.45	5.72	5.30	Not determ.
after disaggregation of particles	5.45	17.14	5.30	The same
Specific surface area, m^2/g	18	70	Not determ.	73
Total cation exchange capacity, mg · equ. per 100 g	3.80	19.52	6.51	16.70
Including:				
Ca^{2+}	Not determ.	14.39	3.60	12.50
Mg^{2+}	The same	4.80	2.72	3.60
Na^+	"	0.30	0.14	0.60

It is found that disordering of the main clay-forming mineral to a large extent affects some physicochemical properties of clays (Table 3). In particular, the disordering of the kaolinite structure in Troshkovskoe kaolinic clays leads to disturbance of bonds around the aluminosilicon units, which together with isomorphic substitution inside the structure causes a shortage of positive charges, which is compensated by exchange cations Na^+, Mg^{2+}, and Ca^{2+} making up the exchange complex. However, the relatively low exchange capacity of minerals in the kaolinite group is accounted by disrupted bonds in the vertical planes parallel to the axis c; moreover, the more disordered the structure and the smaller the particle size, i.e., the lower the degree of crystallization of kaolinite, the higher is its exchange capacity, whereas in the case of montmorillonite minerals, the predominant reason for their increased cation exchange capacity is isomorphism in tetrahedral and especially in octahedral layers, which constitutes around 80% of the total exchange capacity [9]. Knowledge of the type of ionic exchange is especially important for controlling the plastic properties of clays and flow properties of clay suspensions, for instance, in thinning ceramic slip.

The disordering of the structure is also reflected in the behavior of argillaceous minerals in heating. It is noted in [10] that the DTA curves of kaolinite with a disordered structure typically have an exothermic effect within a temperature range of $50 - 200°C$ which is probably due to the extended surface of disordered kaolinite (up to $50 - 70\ m^2/g$), since it is known that the amount of adsorbed water for finely dispersed samples will be much higher and its role will be more significant. Furthermore, it is demonstrated in [11] that the more destroyed the particles are, the higher the peak of the low-temperature water removal. Moreover, the cation exchange capacity of disordered kaolinite increases with increasing specific surface area [9], and the amount of molecular water bound by the exchange cations grows as well [12].

As for montmorillonite, the endothermic reactions on the DTA curves determined by dehydration by montmorillonite vary in intensity and process temperature depending on the type of the substitution cation and the structural unit in which these changes are observed (the tetrahedral or octahedral positions). For instance, the more ferrous varieties (in which aluminum is replaced by iron in the octahedral layer) have a maximum below 600°C. Hectorite, which is rich in magnesium, stops releasing water at a higher temperature (around 800°C) than high-alumina montmorillonite [9].

The degree of ordering of the initial mineral structure influences the formation of mullite as well, i.e., the more ordered the structure, the easier is mullite formation, whereas the more defects emerge in the crystalline structure, the more the mullite-formation process is delayed [13].

The domestic and foreign practical experience indicates that the most important physicochemical and technological properties of argillaceous rocks depend not only on the qualitative and quantitative composition of their finely divided component, but on the composition of the non-argillaceous component as well.

Researcher É. A. Guber at the Silicate Technology Department of the Tomsk Polytechnic University developed an original scheme for identifying material compositions of argillaceous rocks using a rational chemical analysis, which consists of the standard gross chemical analysis and additional chemical analysis of different extracts (aqueous, hydrochloric acid, soda, etc.) for the purpose of extracting total individual minerals or their characteristic part from clay [14].

According to this method, which has been widely tested in numerous studies, a direct analysis determines the chemical composition of the fine fractions, the quantity and composition of exchange cations, water-soluble salts, carbonates, the amorphous component (colloid minerals), and the amount of amorphous silica and free quartz. Using the results of direct measurements, the amount of hydromica is calculated based on the content of non-exchange potassium oxide, and the composition of the main argillaceous mineral is estimated. By subtracting all components obtained by direct measurements and calculations from the chemical composition of the fine fractions of clays, we obtain the quantity and chemical composition of the main argillaceous mineral in the fine fractions. This residue is converted to 100% and the molar ratio of $Al_2O_3 : SiO_2$ is determined. If this ratio is equal to 1 : 2, the mineral belongs to the kaolinite group; if the ratio is 1 : 4, the mineral belongs to the montmorillonite group. It is possible that this residue in a clay with prevalence of montmorillonite may have a ratio of $Al_2O_3 : SiO_2$ less than 4, which may happen when montmorillonite and kaolinite are present simultaneously or in the presence of such minerals of the montmorillonite group as beidellite, which contains less silica than other components of this group.

The type and structure of argillaceous materials are not the only factors that affect the properties of argillaceous rocks; according to contemporary concepts of the structure of argillaceous minerals and the material composition of argillaceous rocks, virtually all clays, besides the crystalline component, contain some x-ray-amorphous material.

There are data in the literature [8, 15, 16] on the formation of colloid shells around argillaceous particles, which can happen either due to the formation of gel-like products of decomposition of parental rocks in the course of clay formation, or as a consequence of disassociation and dissolution of the surface layer of the argillaceous particles in water, or water peptization of hydrophylic clay material.

Both silicic acid sol that is occasionally formed in weathering of feldspar and the surface sol emerging in peptization, whose chemical composition is close to that of argillaceous mineral, are capable of jelly- and gel-formation even with a relatively high water content, as a consequence of skeleton formation by adhesion of the less hydrophilic ends of the argillaceous particles or by adsorption of colloid particles on the surface of the crystallized argillaceous minerals. É. A. Guber concluded that colloids are separated from the crystalline nucleus in heating the fine fraction of clay by a buffer mixture that consists of mixed aqueous solutions of oxalic acid and ammonium oxalate (the Tamm reactant) [14].

These recommendations were used in clarifying the reasons for the kaolinity of some varieties of refractory kaolinite clays (in particular, Troshkovskoe and Katomskoe clays) [4, 5]. It was established that the lack of plasticity of these clays in their natural state is due to the aggregating effect of the amorphous material which cements the clay particles into water-strong aggregates, whose existence is corroborated by electron microscopy. Analysis of the materials composition of the colloids indicated that they contain 70 – 80% colloid aluminum hydroxide $Al(OH)_3$ and gel SiO_2, which in natural conditions exist in the form of aluminosilica gel due to coagulation of oppositely charged particles. Therefore, the properties of such coagulation gel and the strength of its bond to the crystalline nucleus will have a predominant effect on the properties of the argillaceous particle aggregates and finally determine the physicochemical and technological properties of clays.

In the case of the Troshkovskoe kaolinic clays, it is established that their argillaceous particle constitutes a complex aggregate consisting of a crystalline nucleus (kaolinite or halloysite particles with different degrees of hydration) surrounded by a colloid shell. The disordered structure of the argillaceous minerals determine the increased activity of the crystalline nucleus, which, according to the proposed model, takes the form of adsorption of the positively charged aluminosilica gel, which forms the finest shells around the crystalline nuclei (argillaceous particles) and which is firmly fixed due to electrostatic mutual attraction forces. This is presumably the reason for the fact that colloids cannot be isolated from kaolinic clays by simple elutriation.

Along with white-burning refractory and high-melting clays intended for porcelain and faience, low-melting clay and loam with tinted crock after firing are important for ceramics used in construction.

Extensive experimental material accumulated in studying loam materials in Siberia shows that nearly all these rocks are surface loams with a diverse material composition. The mineralogical composition of the fraction over 1 μm has no significant qualitative distinctions; the prevailing minerals are nonplastic ones, such as feldspar (up to 70%), quartz (up to 20%), and others (up to 10%). The finely disperse fraction (below 1 μm) is mostly made up of argillaceous components: a mixture of montmorillonite group minerals in the form of beidellite (60 – 70%) and hydromica of the type of illite (2 – 13%), as well as colloids (14 – 28%), fine-disperse quartz (1 – 7%), and insignificant impurities of other minerals (mainly carbonates).

As for surface loams of the Tomsk Region, it is established that despite their territorial remoteness, they have qualitatively the same material compositions [14]. Furthermore, their main argillaceous mineral is a mineral of the montmorillonite group with the structural formula $\{3H_2O \cdot [(Na, Mg)_{0.02-0.14} \cdot Ca_{0.11-0.30}]_{0.15-0.39}\}(Al_{1.49-1.71} \cdot Fe_{0.18-0.44} \cdot Mg_{0.04-0.27})_2(Si_{4.0-3.51} \cdot Al_{0.49-0.0})_4 \cdot (O_{10.45-9.13} \cdot OH_{2.37-1.51})_{12}$ and the lattice parameters $a = 0.517$ nm, $b = 0.896$ nm, and $c = 1.50$ nm. Isomorphic substitutions are registered in this mineral in both tetrahedral and octahedral layers; furthermore, the aluminum substitution for silicon in the tetrahedral layer in the amount of 3.51 for silicon and 0.49 for aluminum corroborates the opinion of R. Grim [9] who assumed the existence of a natural mineral with a significantly greater substitution than 3.80 and 0.20, respectively, which has been named beidellite. This mineral in the Tomsk Region loam represents a ferrous variety of the montmorillonite group mineral, which is in the phase of transformation from illite to montmorillonite.

In the general case, identification of the structural formula of the main argillaceous mineral makes it possible to predict the behavior of the analyzed rock in technological processing. For instance, the prevalence of Ca^{2+} cation among the exchange cations makes the montmorillonite rock virtually unswellable; in the case of a substantial replacement of the silicon cation Si^{4+} by Al^{3+} in firing one can expect the formation of spinel as one of the high-temperature phase instead of modifications of quartz; isomorphic replacement of Al^{3+} in the octahedral layer by Fe^{2+} and Mg^{2+}, the presence of four-coordination Al^{3+}, as well a substantial replacement of oxygen by the hydroxyl group increase the activity of clay in sintering. Furthermore, the presence of a sufficiently high content of the amorphous component (up to 28%) in the material composition of the Tomsk Region loams also determines their specific behavior in heating. P. G. Usov as early as 1957 attributed their pyrochemical activity (the capacity of making up a mechanically strong product structure as a consequence of solid-state reactions in firing below the sintering temperature, lower than 600 – 700°C) mainly to the composition and the state of colloids which cement the clay particles and facilitate their caking in the solid state [17].

Thus, in selecting argillaceous materials for particular technologies of ceramic production, one should be guided by the integrated evaluation of the properties of the argillaceous rock, such as microaggregation and granulometric and material composition, including the chemical and mineralogical compositions of the argillaceous and impurity components, the presence of amorphous material, and the state of ordering of the clay-forming mineral structure. Knowledge of these properties will make it possible to identify ways of controlling the main technological properties of argillaceous rocks in order to bring them to the required level.

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